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Conversion of rice straw to monomeric phenols under supercritical methanol and ethanol

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HIGHLIGHTS

- Liquefaction of rice straw without any pretreatment is successfully performed.
- High liquid product yield observed (47 wt%).
- Ethanol gave higher yield of liquid product.
- FTIR and NMR showed presence of monomeric phenols.
- GC–MS confirmed phenol and guaiacol derivatives as major products.

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ABSTRACT

Hydrothermal liquefaction of rice straw has been carried out using various organic solvents (CH_3OH, C_2H_5OH) at different temperatures (250, 280 and 300 °C) and residence times (15, 30 and 60 min) to understand the effect of solvent and various reaction parameters on product distribution. Maximum liquid product yield (47.52 wt%) was observed using ethanol at 300 °C and 15 min reaction time. FTIR and NMR (^1H and ^{13}C) of liquid product indicate that lignin in rice straw was converted to various monomeric phenols. GC–MS of the liquid product showed the presence of various phenol and guaiacol derivatives. Main compounds observed in liquid product were phenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol (4-ethylguaiacol), 2,6-dimethoxyphenol (syringol), 2-isopropyl-5-methylphenol (thymol). Powder XRD and SEM of bio-residue showed that rice straw was decomposed to low molecular weight monomeric phenols.

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1. Introduction

Due to the increase in global demand for energy in the transportation sector, carbon dioxide emissions are expected to reach new record high, increasing from 31 Gt in 2011 to approximately 37 Gt in 2035 (IPCC, 2013). As the crude oil is depleting day by day and is not renewable we need alternate sources to meet our demands and to produce chemicals that are not only renewable and sustainable but also environmental friendly. Biomass is an abundant, renewable source of energy which can be utilized for production of fuels and chemicals. Lignocellulosic biomass for bioenergy as well as chemicals production has attracted more interest as they are often readily and locally available in most of the countries. Utilization of lignocellulosic biomass in an economically feasible manner is still a substantial challenge as the composition and cost of biomass feedstocks varies from place to place. Lignocellulose is composed of three major biopolymers, namely cellulose, hemicellulose and lignin (Liu et al., 2014; Ho et al., 2014).

Potential lignocellulosic biomass that could be used for biofuel/chemicals production is either agro-residue or forest-residue. Nearly 600 million tons of agricultural residues have been produced by India annually; out of which, approximately 300 million tons of it remain unused, and is destroyed by open burning (Dobermann and Fairhurst, 2001; Ranjan and Moholkar, 2013). In most countries, rice straw forms a major component of agro-residues, and thus, could be a potential source of feedstock for biofuels production. In the Indian scenario, the total annual production of rice straw is estimated at 97 MMTPA. Out of this, consumption for domestic use and other uses is 27 and 47 MMTPA, respectively. Despite these uses, a large amount of rice straw (22 MMTPA)

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remains unused, and can be a potential feedstock for biofuels/chemicals production (Gadde et al., 2009; Ranjan et al., 2013).

Liquid hydrocarbons appear to be the most attractive and feasible form of transportation fuel and chemicals taking into account the energy density, stability and existing infrastructure. Hydrothermal liquefaction is a viable process for the conversion of lignocellulosic biomass to liquid hydrocarbons as no energy intensive pretreatment step like drying is required and it can utilize the complete carbon content in biomass without any biomass fractionation step (Singh et al., 2013a). Solvents have remarkable effects on the liquefaction process and direct liquefaction of biomass in the presence of water, organic solvents or supercritical fluids has been studied by various researchers (Karagoz et al., 2005; Chumpoo and Prasassarakich, 2010; Miller et al., 1999; Yang et al., 2009). Methanol and ethanol have lower boiling as well as critical points than water. Due to the lower dielectric constants of these solvents, high molecular weight products that are produced as a result of reaction of cellulose and hemicellulose readily dissolve in them (Mazaheri et al., 2010). Liquefaction in organic solvents other than water produces a higher yield of water insoluble oily products which make them promising solvents for the liquefaction of biomass (Zhou et al., 2012).

Hydrothermal liquefaction of lignin to substituted phenols and aromatic ethers was performed using methanol and ethanol at various temperatures (200, 250 and 280 °C) and residence times of 15, 30 and 45 min where maximum liquid product yield of 85% was observed (Singh et al., 2014). Liu and Zhang investigated the liquefaction of pinewood in the presence of various solvents (water, acetone and ethanol) and observed bio-oil yields of 26.5% and 20.0% using ethanol and acetone as solvents, respectively, which was better than the bio-oil produced using water (18.6%) as solvent (Liu and Zhang, 2008). Wheat straw was hydroliquefied at 300 °C for 4 h in ethanol and toluene under hydrogen pressure of 70 bar using 66% $Ni/SiO_2–Al_2O_3$. Yield of hydroliquefied oil obtained was 11.5% and 8% using ethanol and toluene as solvent respectively in catalytic case (Murnieks et al., 2014). Rice stalk (TRS) torrefied at 200, 240, and 280 °C was liquefied using supercritical ethanol at 325 °C and 14–15 MPa for a residence time of 60 min to study the effect of torrefaction. Bio-oil yield gradually decreased from 55.03% of non-torrefied rice stalk to 49.80% of TRS at 200 °C to 38.56% of TRS at 280 °C (Li et al., 2014). Selective conversion of lignin in corncob residue to monophenols was achieved via a two-step process using H_2O–tetrahydrofuran (THF) co-solvent system. Yield of total monophenols reached up to 24.3 wt% under the optimized conditions with 4-ethylphenol (10.5 wt%), 2,6-dimethoxyphenol (6.6 wt%), and 4-ethylguaiacol (4.0 wt%) as predominant products (Jiang et al., 2014).

The existing thermochemical and biochemical methods for utilization of rice straw have certain limitations with respect to low energy efficiency or production of low value bulk chemicals. The novelty of the present investigation is in using rice straw without any pretreatment and to understand the role of organic solvents (methanol and ethanol) on product portfolio. With this background the present study aims to find the alternative routes for production of high value chemicals from rice straw. In the present investigation single step conversion of rice straw to monomeric phenols has been carried out using organic solvents viz. ethanol and methanol. Hydrothermal liquefaction of rice straw was studied at various temperatures (250, 280 and 300 °C) and pressure during the process was autogenous with maximum pressure in the range of 65–100 bar at residence times of 15, 30 and 60 min. Rice straw and its reaction products were analyzed using various physicochemical characterization methods such as TG, Powder X ray Diffraction (XRD), SEM, FTIR, NMR, and GC–MS to understand and confirm the formation of monomeric phenols from rice straw.

2. Materials and experimental procedures

2.1. Materials

Rice straw was collected from Dehradun (Uttrakhand). The calorific value of rice straw was 13.41 MJ kg^{-1}. The elemental composition of rice straw was as follows C (34.11 wt%), H (6.53 wt%), N (0.17 wt%), S (0). Moisture content of rice straw was found to be 11.95%.

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments were conducted in a 50 ml high pressure autoclave (Parr reactor) made of hastelloy at different reaction conditions of temperature and residence time. In a typical hydrothermal liquefaction experiment, the reactor was loaded with rice straw and organic solvent like ethanol/methanol (1:10 by weight). Then the reactor was purged five times with nitrogen to remove the inside air. Reactants were agitated using stirrer (~400 rpm). The temperature was then raised up to desired value and kept for specific time at that reaction temperature. The pressure during the process was autogenous and maximum pressure was in the range of (65–100 bar) under different reaction conditions. After reaction, the reactor was left to cool down to room temperature to remove the reaction products. The gaseous products were vented and the liquid portion was then separated from solid residue using vacuum filtration. The liquid portion thus obtained was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator under reduced pressure. Upon removal of solvent, this fraction was weighed. Solvent insoluble fraction was dried at 80 °C and then weighed, called as bio-residue (Singh et al., 2014). The experiments were repeated two to three times and the deviation of the liquid yields was within 1–2%. The yield of liquid product was calculated on dry and ash free basis.

$$\text{Liquid product yield (wt\%)} = \frac{\text{Weight of liquid product obtained (g)}}{\text{Weight of rice straw (g)}} \times 100$$

2. 3. Analysis of feed and reaction products

Rice straw was analyzed using thermo gravimetric analysis, powder XRD, SEM and FTIR. The liquid product was analyzed using FTIR, NMR (^1H NMR, ^{13}C NMR) and GC–MS. Powder XRD patterns of bio-residues were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu Kα radiation source. Diffraction patterns in the 2–80° region are recorded with a 0.04 step size (step time = 4 s). SEM images have been collected on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB_6) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for SEM has been subjected to disperse on a carbon paper coated adhesive followed by gold coating. TG-DTG of rice straw was carried out on Shimadzu DTG-60 under N_2 flow. The ^{13}C NMR and ^1H NMR spectra of the liquid samples have been recorded in the Bruker Avance 500 plus instrument using $CDCl_3$ as a solvent. The FTIR spectra were recorded on a Nicolet 8700 FTIR spectrometer. The liquid product were analyzed via gas chromatography–mass spectrometry (GC–MS, Agilent 7890B). The carrier gas was He and column flow rate was 1 mL min^{-1}. A HP-1 column (25 m × 0.32 mm × 0.17 μm) was used for the separation. An oven isothermal program was set at 50 °C for 2 min, followed by a heating rate of 5 °C/min to 260 °C for 5 min. The injected volume was 0.4 μL in a splitless mode.

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3. Results and discussion

3.1. Analysis of rice straw

Rice straw kinetic studies were studied using non-isothermal thermogravimetric data of rice straw decomposition in nitrogen atmosphere at six different heating rates of 5–40 °C min^{-1} using several model free kinetic methods. The results showed that the decomposition process exhibited two zones of constant apparent activation energies. The values ranged from 142 to 170 kJ mol^{-1} (E_{avg} = 155.787 kJ mol^{-1}), and 170 to 270 kJ mol^{-1} (E_{avg} = 236.743 kJ/mol) in the conversion range of 5–60% and 61–90% respectively (Mishra and Bhaskar, 2014). FTIR of rice straw showed various peaks corresponding to lignocellulosic biomass components viz. hemicellulose, cellulose and lignin. The typical FTIR spectrum of rice straw showed broad band of the CH, CH_2 stretching at 2920 cm^{-1} and the CH_2 shearing at 1427 cm^{-1} that corresponds to cellulose and hemicellulose molecule. The wavenumbers of 1640, 1427, and 899 cm^{-1} correspond to C=C stretching, CH_2 bending, and C—H in-plane bending respectively, which indicate the presence of lignin (Qian et al., 2007). Band at 3428 and 1513 cm^{-1} corresponds to H-bonded OH stretch and aromatic CH respectively. Aromatic compound group peaks can be seen between 900 cm^{-1} and 650 cm^{-1}. Powder XRD of rice straw showed the peaks observed at 2Θ = 16° and 22° which are identical peaks of cellulose I crystal and correspond to the (1 1 0), and (2 0 0) planes of cellulose (Ishikawat et al., 1998; Singh et al., 2013b).

3.2. Effect of reaction parameters on liquid product yield

Hydrothermal liquefaction of rice straw was performed using organic solvents (methanol and ethanol) at various temperatures (250, 280 and 300 °C) with residence times of 15, 30 and 60 min. Liquid product yield from hydrothermal liquefaction of rice straw using ethanol and methanol is shown in Figs. 1 and 2 respectively. The effect of various reaction parameters on liquid product yield has been explained in the following sections.

3.2.1. Effect of temperature

Reaction temperature plays an important role during hydrothermal liquefaction as solvent behavior changes with temperature. Supercritical point of methanol and ethanol is lower than that of water. Biomass liquefaction behavior in sub-/supercritical water and supercritical alcohol is different because of difference in hydrogen generation activity, reactivity, and solubility of various products in these solvents. Studies have been carried out to understand the effect of temperature on liquid product yield of rice straw under supercritical methanol and ethanol. When hydrothermal liquefaction was carried out using ethanol, yield of liquid product increased with increasing temperature at all residence times of 15, 30 and 60 min. At 15 min residence time, observed liquid product yield was 22.69, 36.88 and 47.52 wt% at temperatures of 250, 280 and 300 °C respectively. On increasing the residence time to 30 min, the observed liquid product yield was 26.95, 34.04 and 44.68 wt% at 250, 280 and 300 °C respectively. The observed liquid product yield at 60 min residence time was 26.95, 39.72 and 45.39 wt% 250, 280 and 300 °C respectively. In case of liquefaction using ethanol maximum liquid product yield (47.52 wt%) was observed at 300 °C and 15 min residence time. Temperature and solvent had a synergetic effect on liquid product yield which may be explained due to increased biomass fragmentations with increase in temperature. When the temperature employed is sufficiently higher than the activation energies for the bond dissociation, biomass depolymerisation is seen to occur. The competition among fragmentation and repolymerization reactions also defines the role of temperature during hydrothermal liquefaction (Akhtar and Amin, 2011). However, with the increase in thermal energy not only the reaction rates are enhanced but reaction mechanisms also vary. Thus lower temperature favors the ionic reactions and higher temperatures promote the formation of radicals by homolytic bond breakage. The solvent prevents both the cross linking reactions and the reverse reactions by diluting the reaction products. Methanol and ethanol act as hydrogen donor solvents that stabilize the radicals formed during bond cleavage (Hui et al., 2010; Xu and Etcheverry, 2008).

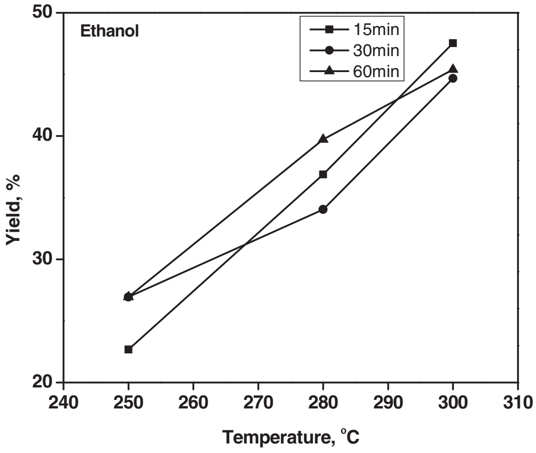

Fig. 1. Effect of residence time and temperature on yield of liquid product obtained from rice straw using ethanol.

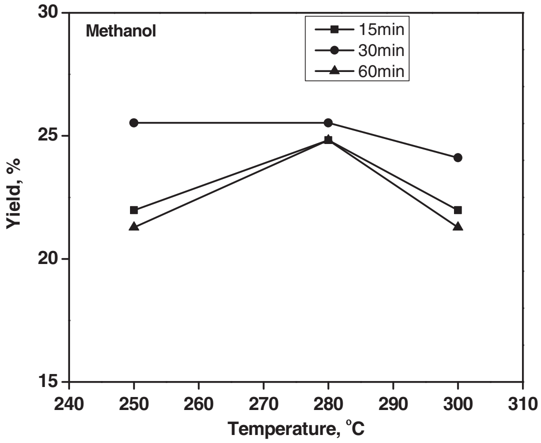

Fig. 2. Effect of residence time and temperature on yield of liquid product obtained from rice straw using methanol.

In case of rice straw liquefaction using methanol as solvent, in general, liquid product yield increased when the temperature was increased from 250 °C to 280 °C and then decreased on further increasing the temperature to 300 °C. At 15 min residence time, observed liquid product yield was 21.98, 24.82 and 21.98 wt% at temperatures of 250, 280 and 300 °C respectively. On increasing the residence time to 30 min, the observed liquid product yield was 25.53, 25.53 and 24.11 wt% at temperatures of 250, 280 and 300 °C respectively. The observed liquid product yield at 60 min residence time was 21.28, 24.82 and 21.28 wt% at temperatures of 250, 280 and 300 °C respectively. There was no significant effect of temperature on liquid product yield. Maximum liquid product yield (25.53 wt%) using methanol was observed at 280 °C and 30 min residence time.

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3.2.2. Effect of residence time

In the present study, residence time did not show much effect on the yield of liquid product. Observed yield of liquid product was almost similar at different residence times at a particular temperature using both ethanol and methanol. In case of liquefaction using ethanol at 250 °C, liquid product yield was observed to be 22.69, 26.95 and 26.95 wt% at residence times of 15, 30 and 60 min respectively. On increasing the temperature to 280 °C, the observed liquid product yield was 36.88, 34.04 and 39.72 wt% at residence times of 15, 30 and 60 min respectively. At 300 °C, observed liquid product yield was 47.52, 44.68 and 45.39 wt% at residence times of 15, 30 and 60 min respectively. Similarly in case of liquefaction using methanol at 250 °C, liquid product yield was 21.98, 25.53 and 21.28 wt% at residence times of 15, 30 and 60 min respectively. On increasing the temperature to 280 °C, the observed liquid product yield was 24.82, 25.53 and 24.82 wt% at residence time of 15, 30 and 60 min respectively. The observed liquid product yield at 300 °C was 21.98, 24.11 and 21.28 wt% at residence times of 15, 30 and 60 min respectively. The reactivity of ethoxy or ethyl groups from ethanol and methyl or methoxy groups from methanol solvent differ at different reaction conditions. Hence the variations in liquid product yield are observed and obtained yields are not similar with different solvent and at different reaction conditions of temperature and residence time.

3.3. Analysis of liquid product

A typical FTIR spectrum of liquid product showed absorbance at 1094, 1210, 1457, 1603, 1696, 2928, 2960, 3370 cm^{-1}. The peaks between 3300 cm^{-1} and 3500 cm^{-1} are characteristic of —OH groups. The absorbances at 2928, 2960 and 1457 cm^{-1} corresponds to C—H stretching vibrations and C—H bending vibrations respectively corresponding to the alkane groups in liquid product. Absorbance of these peaks increased in liquid samples compared to rice straw indicating that rice straw has undergone cleavage to produce liquid product. The absorption peak at around 1700 cm^{-1} suggests the presence of carbonyl groups. The absorbance 1603 cm^{-1} corresponds to aryl groups. Peaks between 950 and 1350 cm^{-1} corresponds to C—O stretch of alcohols and ethers. The peaks at around 1210 and 3370 cm^{-1} indicate the presence of phenols. The peak at 834 cm^{-1} indicates the presence of substituted aromatic groups also observed in our earlier study (Singh et al., 2014). FTIR spectra indicated that lignin in the rice straw samples was decomposed to low molecular weight phenolic compounds. Low activation energy of lignin causes substantial degradation of lignin in hydrothermal medium. Reaction proceeds through the cleavage of aryl ether linkages, fragmentation, and dissolution (Bobleter, 1994). Lignin depolymerisation yields low molecular weight fragments having very reactive functional groups such as syringols, guaiacols, and phenols (Fang et al., 2008).

NMR spectra provided complementary functional group information to FTIR spectra and the ability to quantify and compare integration areas between spectra. A summary of integrated peak area regions assigned to different functional group classes present in the liquid product obtained from hydrothermal liquefaction of rice straw using methanol and ethanol at 15 min residence time are shown in Fig. 3. The region from 0.5 to 3.0 ppm is composed of protons on aliphatic carbon. The region from 0.5 to 1.5 ppm corresponds to protons on aliphatic carbon atoms at least two bonds away from C═C or heteroatom and the region from 1.5 to 3.0 ppm, corresponds to the protons on aliphatic carbon atoms that may be bonded to a C═C double bond or heteroatom. Liquid product obtained from hydrothermal liquefaction of rice straw showed high proton percentage in this region. Around 80% of protons resonate in this region indicating that the liquid product have high aliphatic proton content. In case of liquefaction using methanol at 250 °C, the proton percentage in this region was around 34% and was less compared to other cases. The next portion of the ^{1}H NMR spectrum at 3.0–4.5 ppm represents methoxyl protons (Kosa et al., 2011) or methylene group that joins two aromatic rings. The latter moiety would exist in a partially decomposed lignin oligomer present in the bio-oil (Mullen et al., 2009). In methanol and ethanol case, maximum proton percentage was observed at 250 °C in this region. Proton percentage in this region was higher in methanol than in ethanol case. The region between 4.5 and 6.6 ppm represents aromatic ether protons i.e. lignin derived methoxy phenols. The region of the spectrum between 6.0 and 8.5 ppm corresponds to the aromatic region of spectrum. The liquid product showed significant proton percentage in this region. The liquid product obtained using ethanol as solvent showed higher percentage in this region at higher temperatures. Maximum proton percentage (10%) was observed in this region using ethanol at 280 °C. The downfield spectrum regions (8.5–10 ppm) of the bio-oils arise from the aldehydes and no proton percentage was observed in this region. The FTIR and ^{1}H NMR of the liquid product indicate the presence of substituted monomeric phenols in liquid product obtained.

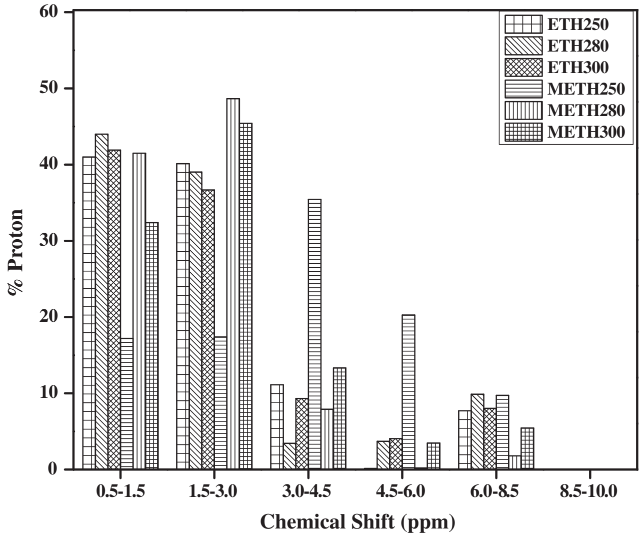

Fig. 3. NMR of liquid product obtained from lignin using ethanol and methanol. ETH250: 250 °C, 15 min, ethanol; ETH280: 280 °C, 15 min, ethanol; ETH300: 300 °C, 15 min, ethanol; METH250:250 °C, 15 min, methanol; METH280: 280 °C, 15 min, methanol; METH 300: 300 °C, 15 min, methanol.

Similar to FTIR and ^{1}H NMR, ^{13}C NMR spectrum of liquid product also showed high aliphatic and aromatic carbon content. A typical ^{13}C NMR spectrum of liquid product obtained at 280 °C and 60 min residence time using ethanol as reaction medium is shown in Supplementary Fig. S1. ^{13}C NMR provided greater detail due to their large chemical shift regions and pointed to a high aliphatic content (0–55 ppm). Around 44% of the carbon atoms resonate in the region from 0 to 55 ppm. This region is further sub divided into two regions, region from 0 to 28 ppm which is composed of short aliphatics and region from 28 to 55 ppm comprising of the long and branched aliphatics. The carbon percentage was higher in region from 0 to 28 ppm (31%) than carbon percentage in region from 28 to 55 ppm (13%). The next region of the spectrum, 55–95 ppm indicates the presence of alcohol ethers and carbohydrate sugars. Carbon percentage was very less in this region (1%). The aromatics and the olefinic compounds resonate in downfield region (95–165 ppm). The carbon percentages in this region was very high (54%). ^{1}H NMR also showed high proton percentage in the aromatic region. FTIR and NMR (^{1}H and ^{13}C) indicated that

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lignin fraction of rice straw was decomposed to low molecular weight monomeric phenols.

The region between 165 and 180 ppm corresponds to the esters and carboxylic acid carbons. Carbon percentage was negligible in this region.

To further understand the composition of liquid product obtained in this study and confirm the findings from FTIR and NMR, GC–MS was carried out which also showed the presence of monomeric phenols. GC–MS also showed the presence of ester compounds like hexadecanoic acid ethyl ester, octadecanoic acid ethyl ester, nonadecanoic acid ethyl ester etc. in liquid product. Such type of ester compounds were also observed in bio-oil obtained from hydrothermal liquefaction of torrified rice stalk in supercritical ethanol (Li et al., 2014). The authors explained that these esters were produced from the esterification between acids and solvent (alcohols). Main compounds observed in liquid product were monomeric phenols that were produced from the decomposition of lignin in rice straw under supercritical methanol and methanol. The amount of phenols observed from rice straw during liquefaction using ethanol was higher than that of methanol. Normalized area percent of selected monomeric phenols obtained from rice straw using ethanol and methanol at various reaction conditions is shown in Tables 1 and 2 respectively.

Composition of liquid product obtained from rice straw using methanol and ethanol is different as reaction medium varies. Also different reaction conditions of temperature and residence time leads to the liquid product with different composition as evident from GC–MS data of liquid product. Main phenolic compounds observed from rice straw using ethanol are phenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol (4-ethylguaiacol), 2,6-dimethoxyphenol (syringol), 2-isopropyl-5-methylphenol (thymol) was also observed in some cases. Mainly substituted phenol and guaiacol derivatives were observed in liquid product. In case of liquefaction using methanol, the main compounds were 4-ethylphenol, dimethylphenol, trimethylphenol, 2-methoxyphenol (guaiacol), 4-ethylguaiacol (4-ethyl-2-methoxyphenol). Phenol was not observed in case of liquefaction using methanol. In case of methanol, methyl substituted phenols and guaiacols were obtained whereas in case of ethanol ethyl substituted phenol and guaiacol derivatives were observed. The formation of such compounds is due to the breakage of various C—C and C—O—C ether bonds (β-O-4 or/and α-O-4) of lignin present in rice straw. The ethanol and methanol may further react to give corresponding methyl and ethyl substituted phenol and guaiacol derivatives. During lignin hydrothermal liquefaction, various reactions like cleavage of the ether and C—C bond, demethoxylation, alkylation and condensation etc. occur. Various linkages like β-O-4 and C_{α}—C_{β} bonds between different lignin monomers were easier to break whereas the aromatic rings were not affected during hydrothermal liquefaction. With increase of temperature demethoxylation and alkylation of lignin derived phenolic compounds occured and various alkyl phenols were formed (Singh et al., 2014; Kang et al., 2013). The present investigation indicated the highly reactive environment created by supercritical ethanol and methanol has facilitated to decompose lignin to monomeric phenols. Similar observations were observed in our study using lignin where also ethanol and methanol played a critical role for the formation of aromatic ethers and phenols (Singh et al., 2014).

3.4. Analysis of solid products

It was observed from powder XRD that bio-residue obtained in the study was almost amorphous. Peaks due to cellulose ($2\Theta = 16°$ and 22°) become week in the bio-residue obtained after the reaction. While comparing SEM images of the rice straw and

Table 1
Monomeric phenols normalized area percentage obtained in liquid product from Rice straw using ethanol at different conditions from GC–MS.

Compound	Area %								
	E1	E2	E3	E4	E5	E6	E7	E8	E9
Phenol	–	9.34	–	1.09	–	–	1.50	1.73	2.13
3-Methyl phenol	1.02	3.37	–	2.64	2.41	–	2.67	2.39	3.80
2-Ethyl phenol	1.25	1.04	2.89	1.82	2.31	–	2.12	1.66	2.91
3-Ethyl phenol	–	–	3.06	–	–	–	–	–	–
4-Ethyl phenol	12.72	12.70	13.65	6.50	7.31	23.48	6.40	4.92	7.60
2-(1-Methylethyl)phenol	1.75	–	3.71	1.83	2.10	–	–	–	–
4-Ethyl-2-methoxyphenol	10.80	9.66	–	4.49	–	–	3.47	1.69	4.52
2,6-Dimethoxy phenol	5.21	4.73	–	–	–	–	–	–	–
2-Methoxy-4-propyl phenol	2.31	2.29	2.34	–	1.81	–	–	–	–
2-Methyl phenol	–	0.98	–	1.46	1.31	–	2.1	2.41	2.63
p-Cresol	–	1.14	–	–	–	–	–	–	–
2,6-Dimethylphenol	–	0.50	–	–	–	–	0.12	0.34	–
2-Ethyl-4-methoxyphenol	–	–	7.39	–	–	–	–	–	–
2-Ethyl-6-methyl phenol	–	–	2.28	1.48	1.84	–	1.68	1.71	8.12
2,4,6-Trimethyl phenol	–	–	–	1.04	–	–	–	0.58	–
3,4,5-Trimethyl phenol	–	–	–	4.41	–	–	–	2.02	–
2-Methyl-4-isopropylphenol	–	–	8.02	–	–	–	–	–	–
3,4-Diethylphenol	–	–	–	–	–	–	–	–	–
6-Tertbutyl-2,4-dimethylphenol	–	–	2.06	–	–	–	0.60	–	–
Thymol	–	–	–	–	–	14.08	–	2.83	–
3,4-Diethylphenol	–	–	2.03	–	–	–	–	–	–
2,5-Dimethylphenol	–	–	–	1.94	2.41	–	1.69	–	2.02
2-Ethyl-4-methylphenol	–	–	–	1.51	–	–	0.91	–	–
3-Methyl-4-isopropylphenol	–	–	–	3.11	–	–	–	–	4.13
2-Ethyl-5-methylphenol	–	–	–	–	1.03	–	3.54	3.23	0.31
2-Ethyl-4,5-dimethylphenol	–	–	–	–	4.32	–	0.40	0.97	1.58
3-(1-Ethylmethyl)phenol	–	–	–	–	–	–	1.17	–	–
1-Ethyl-4-methoxyphenol	–	–	–	–	–	–	1.63	–	–
5-Ethyl-5-n-propyl phenol	–	–	–	–	–	–	1.49	–	–
2,3-Dimethylphenol	–	–	–	–	–	–	–	1.35	0.47
4-Ethyl-3-methylphenol	–	–	–	–	–	–	–	1.51	–

E1: ethanol, 250 °C, 15 min; E2: ethanol, 250 °C, 30 min; E3: ethanol, 250 °C, 60 min; E4: ethanol, 280 °C, 15 min; E5: ethanol, 280 °C, 30 min; E6: ethanol, 280 °C, 60 min; E7: ethanol, 300 °C, 15 min; E8: ethanol, 300 °C, 30 min; E9: ethanol, 300 °C, 60 min.

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Table 2
Monomeric phenols normalized area percentage obtained in liquid product from rice straw using methanol at different conditions from GC–MS.

Compound	Area %								
	M1	M2	M3	M4	M5	M6	M7	M8	M9
2-Ethylphenol	–	–	–	0.53	1.12	–	–	–	–
4-Ethylphenol	15.43	7.73	–	3.11	4.44	3.34	3.77	3.67	3.14
3-Ethylphenol	–	–	–	0.13	–	–	0.46	–	–
2-Methylphenol	–	1.45	1.28	–	–	1.39	–	0.70	–
3-Methylphenol	–	–	–	–	–	0.62	–	–	–
Creosol	–	2.06	–	1.07	0.98	–	–	0.94	–
3,5-Dimethylphenol	–	–	–	2.17	2.92	2.63	3.25	2.32	–
2,5-Dimethylphenol	–	–	–	–	–	1.73	–	–	–
2,6-Dimethylphenol	–	–	–	–	2.03	–	–	1.84	–
2,4-Dimethylphenol	–	–	–	0.27	–	–	–	–	–
2-Ethyl-6-methylphenol	–	–	–	0.39	–	–	–	–	–
2-Ethyl-5-methylphenol	–	2.04	–	–	–	–	1.94	1.15	–
2-Ethyl-4-methylphenol	–	–	2.52	0.38	1.42	–	–	0.63	–
2-Methyl-6-propylphenol	–	–	–	–	0.64	–	–	0.56	–
2,4,6-Trimethylphenol	6.01	–	5.39	3.58	5.54	7.11	8.43	3.98	4.94
2,3,6-Trimethylphenol	–	–	–	0.84	2.18	2.40	–	0.53	–
2,4,5-Trimethylphenol	–	1.87	–	1.35	–	–	2.30	–	3.40
2,3,5-Trimethylphenol	–	1.85	1.95	–	–	2.40	–	–	–
2-Ethyl-4,5-dimethylphenol	–	–	4.25	0.82	–	0.87	6.42	–	4.67
2-Methyl-5(1-methylethyl)phenol	–	–	–	2.44	2.98	–	–	–	–
2-(1-Methylethyl)phenol	–	–	–	–	–	4.09	–	–	–
Thymol	–	–	–	–	–	–	1.57	–	–
3-Methoxy-2,4,6-trimethylphenol	–	–	–	0.77	–	–	–	–	–
2,3,4,6-Tetramethylphenol	9.63	1.13	8.76	4.31	–	–	8.70	3.00	14.41
2,3,5,6-Tetramethylphenol	6.34	–	–	–	–	6.61	4.79	0.90	–
2-Methoxyphenol	–	6.47	–	–	3.37	–	–	2.06	–
2-Methoxy-5-methylphenol	–	–	–	–	4.42	–	–	0.42	–
2-Methoxy-3-methylphenol	–	–	–	–	1.29	–	–	–	–
2-Butylphenol	–	–	–	–	0.74	–	–	–	–
4-Ethyl-2-methoxyphenol	15.16	12.16	–	–	7.79	–	–	–	–
2,6-Dimethoxyphenol	–	4.62	–	–	1.57	–	–	0.91	–
2-Methoxy-4-propylphenol	–	2.08	1.95	–	1.10	–	–	–	–
3-Methyl-4-isopropylphenol	6.03	–	4.72	–	–	3.73	–	–	5.66

M1: methanol, 250 °C, 15 min; M2: methanol, 250 °C, 30 min; M3: methanol, 250 °C, 60 min; M4: methanol, 280 °C, 15 min; M5: methanol, 280 °C, 30 min; M6: methanol, 280 °C, 60 min; M7: methanol, 300 °C, 15 min; M8: methanol, 300 °C, 30 min; M9: methanol, 300 °C, 60 min.

bio-residue obtained, morphological changes were observed. SEM images showed that various components of rice straw have undergone cleavage and bio-residue of spongy and porous nature was observed. Typical SEM image of rice straw and bio-residue obtained is provided as Supplementary information shown in Fig. S2.

4. Conclusions

Hydrothermal liquefaction of rice straw was carried out using methanol and ethanol at different conditions of temperature and residence time. Liquid product yield obtained in case of liquefaction with ethanol was higher than that of methanol. Maximum liquid product yield (47 wt%) was obtained at 300 °C and 15 min residence time using ethanol. Liquid product was mainly composed of alkyl derivatives of phenol and guaiacol. Main compounds observed in liquid product were phenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol (4-ethylguaiacol), 2,6-dimethoxyphenol (syringol), 2-isopropyl-5-methylphenol (thymol). Ethanol proved to be a better solvent than methanol for conversion of rice straw to monomeric phenols.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.01.001.

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